AIP | The Journal of Chemical Physics

Hofmeister effects in micromolar electrolyte solutions

Shinichi Enami, Himanshu Mishra, Michael R. Hoffmann, and Agustín J. Colussi

Citation: J. Chem. Phys. **136**, 154707 (2012); doi: 10.1063/1.4704752
View online: http://dx.doi.org/10.1063/1.4704752
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v136/i15
Published by the American Institute of Physics.

Hofmeister effects in micromolar electrolyte solutions

Shinichi Enami,[1,2,3,a)] Himanshu Mishra,[4,5] Michael R. Hoffmann,[4] and Agustín J. Colussi[4,a)]
[1]*The Hakubi Center, Kyoto University, Kyoto 606-8302, Japan*
[2]*Research Institute for Sustainable Humanosphere, Kyoto University, Uji 611-0011, Japan*
[3]*PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan*
[4]*Ronald and Maxine Linde Center for Global Environmental Science, California Institute of Technology, California 91125, USA*
[5]*Materials Science Department, California Institute of Technology, California 91125, USA*

(Received 30 December 2011; accepted 3 April 2012; published online 19 April 2012)

Ions induce both specific (Hofmeister) and non-specific (Coulomb) effects at aqueous interfaces. More than a century after their discovery, the origin of specific ion effects (SIE) still eludes explanation because the causal electrostatic and non-electrostatic interactions are neither local nor separable. Since direct Coulomb effects essentially vanish below ~10 μM (i.e., at >50 nm average ion separations in water), we decided to investigate whether SIE operate at, hitherto unexplored, lower concentrations. Herein, we report the detection of SIE above ~0.1 μM in experiments where relative iodide/bromide populations, $\chi = I^-/Br^-$, were determined on the surface of aqueous (NaI + NaBr) jets by online electrospray mass spectrometry in the presence of variable XCl (X = H, Na, K, Cs, NH_4, and $N(C_4H_9)_4$) and NaY (Y = OH, Cl, NO_3, and ClO_4) concentrations. We found that (1) all tested electrolytes begin to affect χ below ~1 μM and (2) I^- and Br^- are preferentially suppressed by co-ions closely matching their interfacial affinities. We infer that these phenomena, by falling outside the reach of even the longest ranged electrostatic interactions, are dynamical in nature. [http://dx.doi.org/10.1063/1.4704752]

I. INTRODUCTION

The specific partitioning of ions to water–hydrophobe interfaces underlies important chemical, physical, and biological phenomena.[1–4] Specific ion adsorption at the surface of the ocean is reflected in the distinct composition of marine aerosols[5–8] and its significant impact on the chemistry of the atmospheric boundary layer.[5,9–14] Enzyme activities,[15] protein binding,[16] and self-assembly processes in general[17–22] also show pronounced specific ion effects (SIE). Controlling the self-aggregation of nanoparticles and biopolymers via SIE is a tantalizing goal that calls for a deeper understanding of structural, Coulombic, and non-electrostatic effects at low, intermediate, and high concentrations.[21] It has become apparent that the specificity and range of SIE cannot be explained by merely appending many-body electrodynamic (dipolar and dispersive) forces to electrostatics, as assumed by the classical DLVO (Derjaguin-Landau-Verwey-Overbeek) theory of surface interactions.[4,23–27] The full consequences of quantum fluctuations within extended dielectric media in the presence of charges are being investigated using molecular dynamics simulations,[28] and continuum non-local electrostatics models based on a dielectric function $\varepsilon(\boldsymbol{r}, \boldsymbol{r}')$ of both the local electric field and the long-range polarization of the surrounding medium.[29–31]

A key parameter in models dealing with cooperative effects is the length of correlations, λ, in this case those induced by hydrated ions on the structure of interfacial water. Hitherto an adjustable model parameter, λ should be independently determined by experiments. A recent experimental study has provided evidence of SIE in <50 μM electrolytes (one ion in $>10^6$ water molecules) at a solid/water interface,[4,32] suggesting that the dilution threshold or, equivalently, the limiting value of λ had not been reached. The operation of unidentified long-range interactions on the surface of electrolyte solutions had been surmised from the surface tension minima observed in electrolyte solutions at ~1 mM.[33–35] Seventy-five years ago, Dole realized that a model that invoked electrostatic interactions among ions that saturate the surface of water at ~1 mM could formally account for such minima, but was physically implausible. He conjectured that "some other (unknown) factor such as an electric effect (by ions on the solvent)" was involved.[33] The fact that Dole's "unknown" factor remains to be characterized points to a phenomenon whose interpretation might require new perspectives.

We recently exploited the high sensitivity, surface selectivity, and unambiguous identification capabilities of online electrospray mass spectrometry (ESMS) (see below)[36,37] to investigate SIE on the surface of electrolyte solutions at low concentrations (see the EXPERIMENTAL SECTION and Figure S1 in the supplemental information, (SI)).[38] ESMS is conventionally used to investigate the composition of bulk liquids.[39] However, we have demonstrated that by changing the instrumental configuration and operating parameters it is possible to selectively sample the interfacial layers of liquid jets under ambient temperature and pressure conditions.[5,36,37,40–42] An inherent challenge in studying

a)Authors to whom correspondence should be addressed. Electronic addresses: enami.shinichi.3r@kyoto-u.ac.jp and ajcoluss@caltech.edu.

liquid surfaces is that, because of the relatively small surface-to-volume ratios prevalent in most experiments, they are easily contaminated. Present experiments should be minimally influenced by contamination because they (1) are performed on fast-flowing, continually refreshed water jets (2) monitor simultaneously the ions whose ratio, $\chi = I^-/Br^-$, is the reported observable (see below). We had validated the claim that the mass spectra obtained in our instrumental configuration reflect the ion composition of the outermost layers of the jet by showing that: (1) relative anion abundances, i.e., relative mass spectral signal intensities, measured in jets consisting of *equimolar* multi-electrolyte solutions follow a normal Hofmeister series[6,7,43] and are specifically affected by added cationic or anionic surfactants[6,42] and (2) our mass spectra reveal the presence of products necessarily formed in the air–water layers of jets exposed to reactive gases.[36,37,40,41,44] Herein, we report relative iodide/bromide ion abundances, $\chi = I^-/Br^-$, in air–water interfacial layers of mixed electrolyte solutions in the sub-μM to ~1 mM range.

II. EXPERIMENTAL SECTION

Our experiments involve the injection of aqueous electrolyte solutions as jets into the spraying chamber of an electrospray mass spectrometer (ESMS, Agilent 6130 Quadrupole LC/MS Electrospray System, Kyoto University) held at 1 atm and 298 K. The ion composition of the outermost layers of the jet is monitored *in situ* via online mass spectrometry, after the electroneutral jets are nebulized by an annular coaxial nebulizer gas into droplets possessing net charge of either sign. The excess anions (i.e., the fraction lacking balancing counterions) carried by the negatively charged droplets are ultimately ejected to the gas phase and become amenable to mass spectrometric detection.[45] The present experimental setup is essentially the same as that reported in previous studies from our group.[36,37,41,42] Iodide and bromide ions already present on the surface of the injected liquid are monitored and quantified by online ESMS in less than a few milliseconds. Solutions are pumped (100 μl min^{-1}) into the spraying chamber through a grounded stainless steel needle (100 μm bore) coaxial with a sheath issuing nebulizer N_2(g) at high flow rates. The fast nebulizer gas strips the interfacial layers of the much slower liquid jet into microdroplets that carry excess anions or cations. Note that the production of charged microdroplets from a neutral liquid is the normal outcome of the charge fluctuations expected in a statistical breakup process.[39,46–48] Thus, droplet charging via nebulization does not require the application of an external electric bias to the needle, as in classic ("Taylor cone") electrospray mass spectrometry.[49] Charged microdroplets subsequently evaporate solvent while being drawn to the electrically polarized inlet of the mass spectrometer with increasing acceleration. Since sampled microdroplets are the progeny of the nascent droplets stripped from the surface of the jet, they are naturally enriched with interfacial species. We had previously verified that this setup operates as a quasi-linear transfer device, that is, ESMS signals are directly proportional to ion concentrations (up to ~0.1 mM) prior to their breakup, in experiments in which we monitored the acid–base equilibrium of dissolved tri-methyl-ammonium as a function of bulk *p*H.[36,42] We have also presented detailed data analysis, based on mass balances and the application of the kinetic theory of gases to fast gas–liquid reactions, which strongly suggest (but do not conclusively prove) that the thickness of the interfacial layers sampled in these experiments is likely less than one nm, and certainly within a few nm.[36] Further experimental details and validation tests could be found in the SI and previous publications.[36,37,41,42]

III. RESULTS AND DISCUSSION

Anions generally approach the air–water interface closer than cations. This is borne out by the negative surface potential of most electrolyte solutions,[50,51] by surface-specific spectroscopic studies,[34,52–54] and by model calculations.[2,55–58] A recent phase-sensitive sum-frequency vibrational spectroscopy (PS-SFVS) study reported interfacial ion affinities in the order $I^- > NO_3^- > NH_4^+ > Cl^- > K^+ > Na^+$ between 1 M and 2 M.[54]

Figure 1 shows the negative ion ES mass spectra obtained from 1 μM equimolar (NaI + NaBr) aqueous solutions in the absence and presence of 10, 100, and 1000 μM NaCl. It is apparent that: (1) the population of I^- in the interfacial layers, P_{127}, as reported by $m/z = 127$ signal intensities, is about three times larger (more precisely 3.04 ± 0.24 times, the average of 15 independent measurements) than that of Br^-, P_{79+81}, i.e., the sum of $m/z = 79$ and 81 signal intensities, confirming previous reports by Cheng *et al.*[6,7] and (2) both P_{127} and P_{79+81} decrease with increasing NaCl concentrations. The larger interfacial affinity of iodide relative to bromide is consistent with a number of previous independent experimental results and theoretical predictions.[34,52,57,59,60]

Figure 2 shows how both P_{127} and P_{79+81} decrease in the presence of increasing concentrations of XCl, where X is H, Na, K, Cs, NH_4, or $N(C_4H_9)_4$. Note that the surfactant $N(C_4H_9)_4^+$ has the largest depressing effect on both P_{127} and P_{79+81}, which decrease by 50% upon addition of ~11 μM and ~20 μM $N(C_4H_9)_4Cl$, respectively. Similar effects require the addition of ~110 μM and ~70 μM NaCl, respectively.

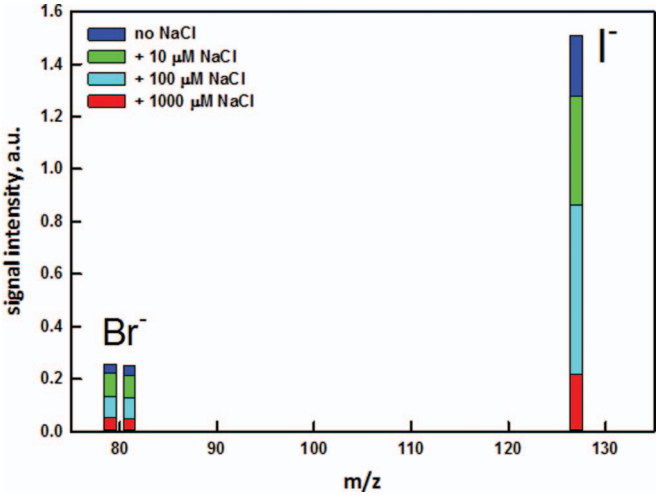

FIG. 1. Negative ion ES mass spectra from aqueous (1 μM NaI + 1 μM NaBr) jets before and after adding 10, 100, and 1000 μM NaCl.

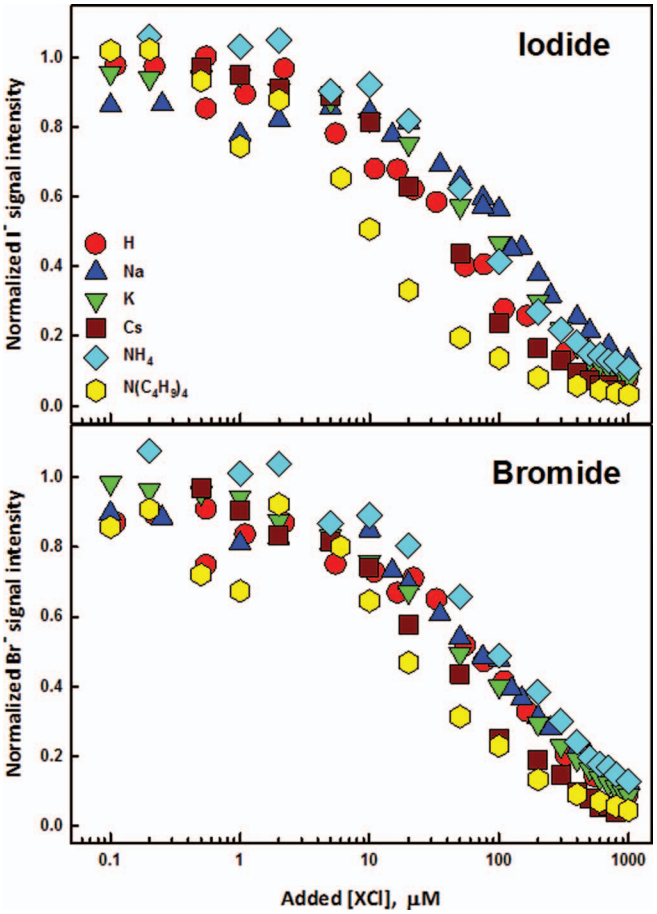

FIG. 2. Semi-logarithmic plots of normalized I^- (upper panel) and Br^- (lower panel) ES mass spectral signal intensities from aqueous (1 μM NaI + 1 μM NaBr) jets as a function of added XCl concentrations. X ≡ H, Na, K, Cs, NH_4, or $N(C_4H_9)_4$.

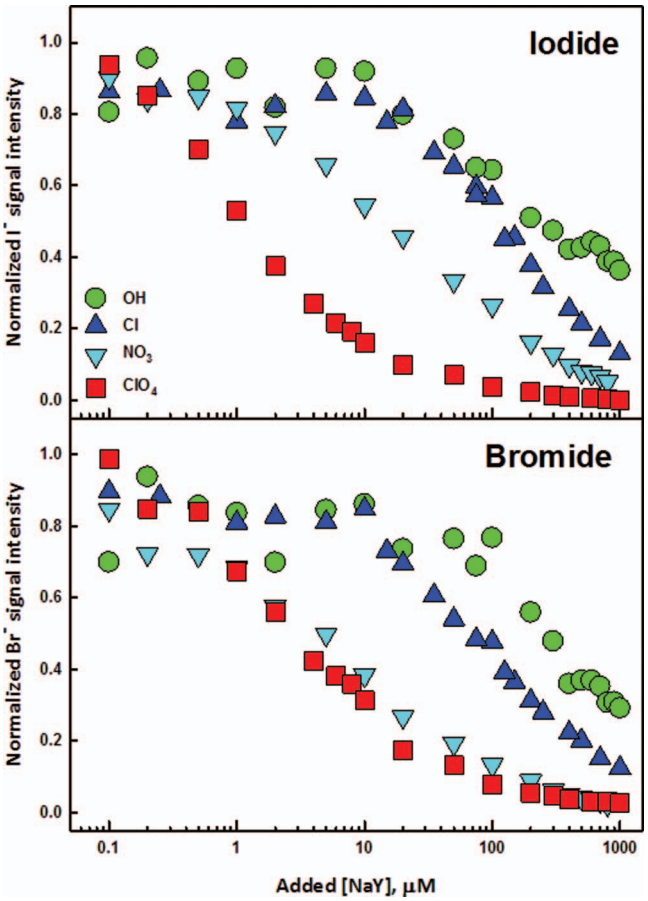

FIG. 3. Semi-logarithmic plots of normalized I^- (upper panel) and Br^- (lower panel) ES mass spectral signal intensities from aqueous (1 μM NaI + 1 μM NaBr) jets as a function of added NaY concentrations. Y ≡ OH, Cl, NO_3, or ClO_4.

Interestingly, the depressing efficiencies of the large Cs^+ and of the small, non-polarizable H^+ (or H_3O^+) on P_{127} are found to be similar.

Figure 3 shows the specificity of co-ion effects upon addition of NaY, where Y = OH, Cl, NO_3, and ClO_4. It is immediately apparent that anions induce both larger and more specific effects than cations, in accord with the Hofmeister effects observed in most phenomena.[4,16,61,62] Note that among the anions studied, ClO_4^- and OH^- have the strongest and weakest effects, respectively: P_{127} is halved by ~1 μM $NaClO_4$ and ~230 μM NaOH. The weak effect of OH^- on interfacial ion populations is particularly intriguing because the negative potential of the air–water interface has been ascribed to strong OH^- adsorption to water–hydrophobe interfaces in general.[51,63,64]

Figure 4(a), which displays the ratio $\chi = P_{127}/P_{79+81} = I^-/Br^-$ as a function of NaY concentrations, reveals that ClO_4^- and NO_3^- have the largest depressing effects on P_{127} and P_{79+81}, respectively. From the relative affinities of Br^- ($f \equiv 1.0$), NO_3^- ($f = 1.4$), I^- ($f = 3.1$), and ClO_4^- ($f = 19$) for the air–water interface (previously measured in a similar setup),[6] we infer that I^- and Br^- are preferentially suppressed by those anions closely matching their interfacial affinities. Present results are in qualitative agreement with the PS-SFVS results showing that $f(Cl^-) < f(NO_3^-) < f(I^-)$.[54] χ is also a function of (NaI + NaBr) concentration, displaying a broad minimum at ~50 μM, in the absence of added electrolytes (Figure S2). Counterions also have significant specific effects on χ (Figure 4(b)). The significant depressing effect of tetrabutyl-ammonium chloride on χ (Figure 4(b)) is consistent with previous findings by Cheng *et al.* that the cetyl-trimethyl ammonium chloride cationic surfactant strongly enhances the interfacial populations of Br^- and NO_3^- without affecting that of I^-.[6] Notably, the depressing efficiency of the small H^+ (or H_3O^+) on χ is similar to that of the large surfactant $N(C_4H_9)_4^+$. We found that neither P_{127} and P_{79+81} nor χ are affected by the addition of up to 1.3 mM 2-propanol.

We had previously proposed, on the basis of the strict exponential dependence of relative anion affinities on ion radius (rather than ion polarizability) observed in our experiments,[6,7] that anions, by having a dielectric permittivity lower than the solvent but higher than air: $\varepsilon_W > \varepsilon_{ion} > 1$, are necessarily rejected to the air–water interface by many-body electrodynamic interactions.[26,27,51,65] However, since $\varepsilon_W(z)$ is not a monotonic but oscillating function of depth z, displaying both positive and negative values separated by sharp discontinuities within 0.5 nm of the interface,[29,66–68] interfacial ion distributions should not be expected to be monotonic or even continuous functions of depth.[66] From this standpoint, relative ion affinities would reflect the dissimilar depths, z_i, at which

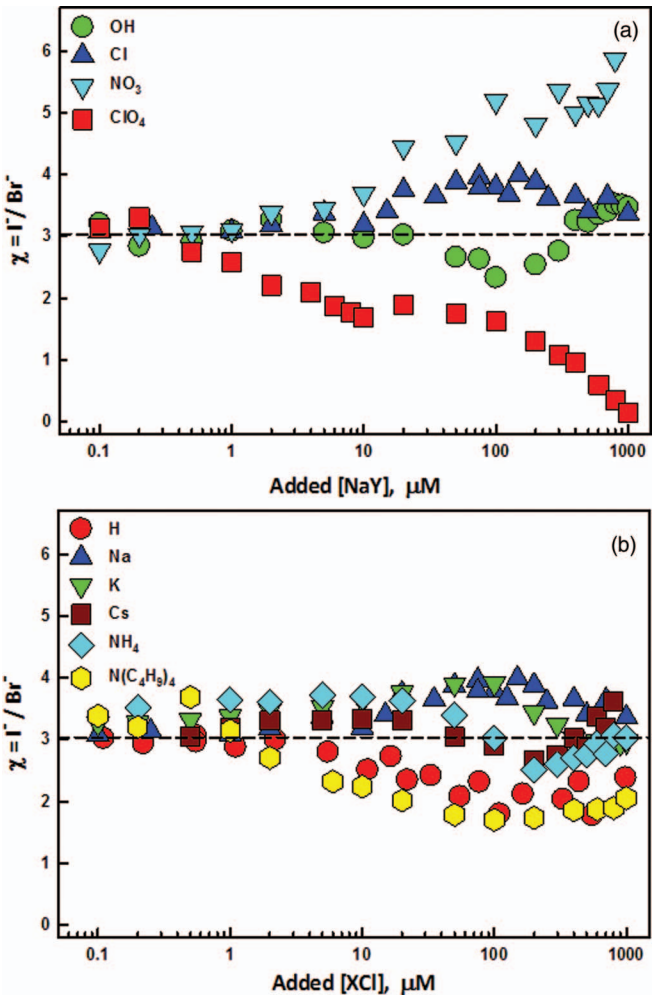

FIG. 4. Semi-logarithmic plots of the ratio of ES mass spectral signal intensities $\chi = I^-/Br^-$ from aqueous (1 μM NaI + 1 μM NaBr) jets as a function of added NaY (Y ≡ OH, Cl, NO_3, or ClO_4) (a) and XCl (X ≡ H, Na, K, Cs, NH_4 or $N(C_4H_9)_4$) (b) concentrations. Dashed horizontal lines correspond to $\chi(0) = 3.04 \pm 0.24$.

ions balance the electrodynamic forces driving them to the interface with the entropic losses associated with the creation of interfacial concentration gradients. Thus, different ions are envisioned to populate interfacial layers of different depths, z, rather than a common interfacial region with different probabilities, as confirmed by the charge-specific effects induced by cationic versus anionic surfactants.[6,14,42]

The similar effects of H^+ and $N(C_4H_9)_4^+$ on χ therefore suggest that H^+, *once it emerges to the surface* at *p*H < 4,[36,37,42] reaches interfacial layers of depths intermediate between those occupied by I^- and Br^-. We have previously shown that gaseous trimethylamine is protonated in collisions with aqueous jets only at *p*H < 4.[36,42] Thus, present results confirm that H^+ becomes available in the outermost layers below *p*H ~ 4.[36,37,42] Our results, by showing that OH^- barely affects I^- or Br^-, in contradistinction with NO_3^- or ClO_4^-, indicate that OH^- *from NaOH* does not reach the outermost interfacial layers sampled herein. This conclusion may be consistent with a recent analysis of surface tension data showing that the surface-to-bulk partitioning ratios are in the order $H^+ > Li^+ \sim K^+ \sim Na^+$ in XCl and $I^- > NO_3^- > Br^- > OH^-$ in NaY.[69] However, it should be pointed out that OH^-, as an intrinsic ion at aqueous interfaces, may not conform to the pattern established by other anions. Whether and under what conditions OH^- becomes available to gaseous acids at the air–water is the subject of an upcoming report from our group.[70] Summing up, the results of Figure 4 represent compelling evidence of specific interactions among ions at the air–water interface down to the hitherto unexplored submicromolar range.

It should be realized the observed SIE in micromolar electrolyte solutions cannot be solely accounted for by electrostatic interactions across rigid dielectric interfacial water layers.[71] In the <1 μM solutions studied herein, the average ion–ion separations $\langle R_{\text{ion–ion}} \rangle > 120$ nm significantly exceeds the Bjerrum length (i.e., the separation at which the electrostatic energy of an ion pair becomes commensurate with thermal energy): $\lambda_B = e^2/(4\pi\varepsilon_0\varepsilon k_B T) = 56$ nm in vacuum ($\varepsilon = 1$).[27] Furthermore, the requisite interactions must also carry specific chemical information over long ranges. Although definitive explanation may not be provided at this time, it is conceivable that such interactions could be propagated by thermal capillary waves (CW), which are powered by the thermal surroundings and span broad frequency ω_{CW} and wavelength λ_{CW} domains.[71–76] Recent simulations have shown that anions specifically bias surface height fluctuations several molecular diameters away by pinning thermal capillary waves.[77] The preceding dipole moments of water molecules bound to interfacial anions that, in contrast with those bound to cations, generate oscillating fields parallel to the surface might be an essential feature of the propagation mechanism.[78,79]

IV. CONCLUSIONS

We found that the populations of I^- and Br^- on the surface of equimolar 1 μM (NaI + NaBr) solutions are significantly and specifically affected by the presence of various NaY and XCl electrolytes in the 0.1 μM to 10^3 μM range. Our results represent clear evidence that Hofmeister effects operate even in sub-micromolar electrolyte solutions. The specificity of the observed effects indicates that I^- and Br^- are suppressed more strongly by those ions having similar interfacial affinities, e.g., I^- by ClO_4^- and Br^- by NO_3^-. Remarkably, H^+ and the cationic surfactant $N(C_4H_9)_4^+$ have similar effects on $\chi = I^-/Br^-$, whereas OH^- has none. We infer that these phenomena, because they fall outside the reach of even the longest ranged electrostatic forces, are dynamical in essence. Given the importance and universality of Hofmeister effects across many fields, present findings may have deep implications for understanding specificity in biology and chemistry at aqueous interfaces.

ACKNOWLEDGMENTS

This work was financially supported by the Japan Science and Technology Agency (JST) PRESTO program. We are grateful to Dr. Drew Parsons and Professor Barry Ninham for a helpful discussion. S.E. is grateful to Professor K. Takahashi, Professor M. Shiotani, and Ms. A. Hatano of

Kyoto University for assisting the startup of a new laboratory. Valuable discussions with Professor William Goddard and Dr. Tod Pascal of California Institute of Technology are also acknowledged.

[1]P. B. Petersen and R. J. Saykally, Annu. Rev. Phys. Chem. **57**, 333 (2006).
[2]P. Jungwirth and D. J. Tobias, Chem. Rev. **106**, 1259 (2006).
[3]L. S. McCarty and G. M. Whitesides, Angew. Chem., Int. Ed. **47**(12), 2188 (2008).
[4]D. F. Parsons, M. Bostrom, P. Lo Nostro, and B. W. Ninham, Phys. Chem. Chem. Phys. **13**(27), 12352 (2011).
[5]S. Enami, C. D. Vecitis, J. Cheng, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. A **111**, 8749 (2007).
[6]J. Cheng, C. Vecitis, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. B **110**, 25598 (2006).
[7]J. Cheng, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. B **112**, 7157 (2008).
[8]P. S. Liss and R. A. Duce, *The Sea Surface and Global Change* (Cambridge University Press, Cambridge, 1997).
[9]P. Davidovits, C. E. Kolb, L. R. Williams, J. T. Jayne, and D. R. Worsnop, Chem. Rev. **106**, 1323 (2006).
[10]B. J. Finlayson-Pitts, Phys. Chem. Chem. Phys. **11**(36), 7760 (2009).
[11]E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub, and B. J. Finlayson-Pitts, Science **288**(5464), 301 (2000).
[12]D. J. Donaldson and K. T. Valsaraj, Environ. Sci. Technol. **44**(3), 865 (2010).
[13]S. Hayase, A. Yabushita, M. Kawasaki, S. Enami, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. A **115**(19), 4935 (2011).
[14]T. Kinugawa, S. Enami, A. Yabushita, M. Kawasaki, M. R. Hoffmann, and A. J. Colussi, Phys. Chem. Chem. Phys. **13**(11), 5144 (2011).
[15]M. C. Pinna, P. Bauduin, D. Touraud, M. Monduzzi, B. W. Ninham, and W. Kunz, J. Phys. Chem. B **109**(34), 16511 (2005).
[16]L. M. Pegram, T. Wendorff, R. Erdmann, I. Shkel, D. Bellissimo, D. J. Felitsky, and M. T. Record, Proc. Natl. Acad. Sci. U.S.A. **107**(17), 7716 (2010).
[17]E. Leontidis, Curr. Opin. Colloid Interface Sci. **7**(1–2), 81 (2002).
[18]L. J. Han, S. J. Hyung, J. J. S. Mayers, and B. T. Ruotolo, J. Am. Chem. Soc. **133**(29), 11358 (2011).
[19]X. F. Li, S. Lettieri, N. Wentzel, and J. D. Gunton, J. Chem. Phys. **129**(16), 164113 (2008).
[20]B. C. Gibb, Isr. J. Chem. **51**(7), 798 (2011).
[21]B. W. Ninham and P. Lo Nostro, *Molecular Forces and Self Assembly* (Cambridge University Press, Cambridge, 2010).
[22]N. Schelero and R. von Klitzing, Soft Matter **7**(6), 2936 (2011).
[23]W. Kunz, P. Lo Nostro, and B. W. Ninham, Curr. Opin. Colloid Interface Sci. **9**, 1 (2004).
[24]V. V. Yaminsky and B. W. Ninham, Adv. Colloid Interface Sci. **83**(1–3), 227 (1999).
[25]J. K. Beattie, Chem. Phys. Lett. **481**(1–3), 17 (2009).
[26]I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. **10**, 165 (1961).
[27]J. Israelachvilii, *Intermolecular & Surface Forces*, 3rd ed. (Academic, London, 2011).
[28]R. C. Remsing, J. M. Rodgers, and J. D. Weeks, J. Stat. Phys. **145**(2), 313 (2011).
[29]D. J. Bonthuis, S. Gekle, and R. R. Netz, Phys. Rev. Lett. **107**(16), 166102 (2011).
[30]D. Ben-Yaakov, D. Andelman, and R. Podgornik, J. Chem. Phys. **134**(7), 074705 (2011).
[31]A. Hildebrandt, R. Blossey, S. Rjasanow, O. Kohlbacher, and H. P. Lenhof, Phys. Rev. Lett. **93**, 108104 (2004).
[32]J. M. Borah, S. Mahiuddin, N. Sarma, D. F. Parsons, and B. W. Ninham, Langmuir **27**(14), 8710 (2011).
[33]M. Dole, J. Am. Chem. Soc. **60**, 904 (1938).
[34]P. B. Petersen and R. J. Saykally, J. Am. Chem Soc. **127**, 15446 (2006).
[35]G. Jones and W. A. Ray, J. Am. Chem. Soc. **59**, 187 (1937).
[36]S. Enami, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. Lett. **1**(10), 1599 (2010).
[37]S. Enami, L. A. Stewart, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. Lett. **1**(24), 3488 (2010).
[38]See supplementary material at http://dx.doi.org/10.1063/1.4704752 for a description of the experimental technique.
[39]I. Manisali, D. D. Y. Chen, and B. B. Schneider, TrAC, Trends Anal. Chem.. **25**, 243 (2006).
[40]S. Enami, M. R. Hoffmann, and A. J. Colussi, Proc. Natl. Acad. Sci. U.S.A. **105**(21), 7365 (2008).
[41]S. Enami, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. Lett. **1**(15), 2374 (2010).
[42]S. Enami, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. A **114**(18), 5817 (2010).
[43]E. Psillakis, J. Cheng, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. A **113**(31), 8826 (2009).
[44]S. Enami, M. R. Hoffmann, and A. J. Colussi, J. Phys. Chem. B **113**(23), 7977 (2009).
[45]J. V. Iribarne and B. A. Thomson, J. Chem. Phys. **64**, 2287 (1976).
[46]A. Hirabayashi, M. Sakairi, and H. Koizumi, Anal. Chem. **66**(24), 4557 (1994).
[47]A. Hirabayashi, M. Sakairi, and H. Koizumi, Anal. Chem. **67**(17), 2878 (1995).
[48]L. W. Zilch, J. T. Maze, J. W. Smith, G. E. Ewing, and M. F. Jarrold, J. Phys. Chem. A **112**(51), 13352 (2008).
[49]S. Nguyen and J. B. Fenn, Proc. Natl. Acad. Sci. U.S.A. **104**(4), 1111 (2007).
[50]N. L. Jarvis and M. A. Scheiman, J. Phys. Chem. **72**(1), 74 (1968).
[51]A. Gray-Weale and J. K. Beattie, Phys. Chem. Chem. Phys. **11**(46), 10994 (2009).
[52]P. B. Petersen and R. J. Saykally, Chem. Phys. Lett. **397**(1–3), 51 (2004).
[53]C. S. Tian and Y. R. Shen, Proc. Natl. Acad. Sci. U.S.A. **106**(36), 15148 (2009).
[54]C. S. Tian, S. J. Byrnes, H. L. Han, and Y. R. Shen, J. Phys. Chem. Lett. **2**(15), 1946 (2011).
[55]K. N. Kudin and R. Car, J. Am. Chem. Soc. **130**(12), 3915 (2008).
[56]C. D. Wick and L. X. Dang, J. Chem. Phys. **133**(2), 024705 (2010).
[57]M. D. Baer and C. J. Mundy, J. Phys. Chem. Lett. **2**(9), 1088 (2011).
[58]D. Ben-Amotz, J. Phys. Chem. Lett. **2**(10), 1216 (2011).
[59]S. Ghosal, J. C. Hemminger, H. Bluhm, B. S. Mun, E. L. D. Hebenstreit, G. Ketteler, D. F. Ogletree, F. G. Requejo, and M. Salmeron, Science **307**, 563 (2005).
[60]P. Jungwirth and D. J. Tobias, J. Phys. Chem. B **106**(25), 6361 (2002).
[61]F. Hofmeister, Arch. Exp. Pathol. Pharmakol. (Leipzig) **24**, 247 (1888).
[62]K. D. Collins and M. W. Washabaugh, Q. Rev. Biophys. **18**, 323 (1985).
[63]J. K. Beattie, A. N. Djerdjev, and G. G. Warr, Faraday Discuss. **141**, 31 (2009).
[64]P. Creux, J. Lachaise, A. Graciaa, J. K. Beattie, and A. M. Djerdjev, J. Phys. Chem. B **113**(43), 14146 (2009).
[65]V. A. Parsegian, *Van der Waals Forces* (Cambridge University Press, New York, 2006).
[66]R. Podgornik and V. A. Parsegian, J. Chem. Phys. **121**(15), 7467 (2004).
[67]M. V. Fedorov and A. A. Kornyshev, Mol. Phys. **105**(1), 1 (2007).
[68]T. G. Philbin, C. Xiong, and U. Leonhardt, Ann. Phys. (N.Y.) **325**(3), 579 (2010).
[69]L. M. Pegram and M. T. Record, Proc. Natl. Acad. Sci. U.S.A. **103**, 14278 (2006).
[70]S. Enami, H. Mishra, M. R. Hoffmann, and A. J. Colussi, "Experimental Brønsted basicity of the air-water interface" (to be published).
[71]J. B. Klauda, X. W. Wu, R. W. Pastor, and B. R. Brooks, J. Phys. Chem. B **111**(17), 4393 (2007).
[72]F. Behroozi and N. Podolefsky, Eur. J. Phys. **22**(3), 225 (2001).
[73]C. Fradin, A. Braslau, D. Luzet, D. Smilgies, M. Alba, N. Boudet, K. Mecke, and J. Daillant, Nature (London) **403**(6772), 871 (2000).
[74]A. P. Willard and D. Chandler, J. Phys. Chem. B **114**(5), 1954 (2010).
[75]J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford University Press, New York, 1989).
[76]D. Aarts, M. Schmidt, and H. N. W. Lekkerkerker, Science **304**(5672), 847 (2004).
[77]D. E. Otten, P. R. Shaffer, P. L. Geissler, and R. J. Saykally, Proc. Natl. Acad. Sci. U.S.A. **109**(3), 701 (2012).
[78]K. J. Tielrooij, S. T. van der Post, J. Hunger, M. Bonn, and H. J. Bakker, J. Phys. Chem. B **115**(43), 12638 (2011).
[79]D. L. Cheung, J. Chem. Phys. **135**(5), 054704 (2011).